



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
NATIONAL EXPOSURE RESEARCH LABORATORY
CINCINNATI, OH 45268

OFFICE OF
RESEARCH AND DEVELOPMENT

May 5, 2003

MEMORANDUM

SUBJECT: Perchlorate Analytical Methods Update

FROM: Elizabeth Hedrick, M.S., Research Chemist /s/ EJH
Microbiological and Chemical Exposure
Assessment Research Division (MD-564)

TO: Kevin Mayer, Region 9 Perchlorate Coordinator
Region 9, SFD-7-2

Prior to the 1990s the analytical chemistry methods for the determination of perchlorate anion were based on gravimetric, derivatization/spectrophotometric or electrochemical methods.^{1,2} In the 1990s, separation methods such as ion chromatography and capillary electrophoresis began to dominate. Ion chromatography appears to be the most popular separation techniques, and is amenable to various types of detectors.

The first ion chromatography method using conductivity detection was developed by the California Department of Health Services (CADHS) in 1997.³ They used an anion exchange column with a mobile phase of NaOH/p-cyanophenol and conductivity suppression. The practical quantifiable limit, determined in multi-laboratory study in 1998, was 6 ppb. Later, better columns for separating large polarizable anions like perchlorate were developed and, in 1999, the U.S. EPA published Method 314.0 which uses this next generation of anion exchange resin, electrolytic conductivity suppression and conductivity detection.^{4,5} The detection limit (DL) of Method 314.0 is 0.53 ppb with a widely achievable minimum reporting limit (MRL) of 4 ppb. Through several simple modifications, however, there are labs achieving lower DLs and MRLs using Method 314.0.^{6,7} The modifications being used are (1) large volume injection (2 mL or more), (2) sample preconcentration onto short chromatography columns prior to separation on the analytical column, (3) sample concentration by evaporation and/or (4) dedication of IC instrumentation to low-level perchlorate analysis. Generally, the improvements have resulted in MRLs of approximately 1 ppb. It is important to keep in mind that even though these modifications have worked well for relatively clean and well characterized water samples, there is no data to confirm that these modifications work well for a wide range of sample types. Therefore, these modifications should only be made in specialized circumstances and are not appropriate for general monitoring. For samples containing high concentrations of anions (Cl^- , NO_3^- , CO_3^{2-} , SO_4^{2-}) that elute just prior to perchlorate, further improvements in DLs and MRLs have been possible using sample clean-up procedures. Removal of highly conducting common anions allows perchlorate to elute on a baseline of low conductivity,

further improving detection limits by conductivity. Sample clean-up is typically accomplished with syringe cartridges that contain a resin with ion exchange sites to precipitate or complex the interfering anions. For example, to remove sulfate, a barium-containing resin would be used. Silver ion is used to precipitate Cl^- and H^+ exchange resin is used to remove CO_3^{2-} . The main disadvantage to developing methods dependent on these cartridges to achieve desirable MRLs is cost. Depending on the number of cartridges required, the cost per analysis could increase from \$8-\$24. Currently, there is research underway to develop a resin capable of selectively retaining perchlorate anion in the presence of high concentrations of other anions. If successful, this would provide a means of concentrating perchlorate to achieve lower detection limits in low to high ionic matrices.

Despite the noteworthy advances that have been made in column design for ion chromatography and the advances in sample pre-treatment, there is still the issue of specificity when using conductivity detection. Since perchlorate is identified solely by retention time, there is the potential for misidentification of contaminant peaks in the same retention time window as perchlorate. In most cases, spiking the suspect sample with perchlorate is sufficient to establish the precise retention time of perchlorate in the matrix, and reveals whether or not a suspect peak is indeed perchlorate. Dionex Corporation has made a prototype column for perchlorate that is under investigation at the EPA in Cincinnati. The chemistry of perchlorate retention on this column is completely different from the principle of anion exchange used in Method 314.0, so it shows promise of providing confirmation of perchlorate using conductivity detection.

However, an ideal detector would utilize unique and specific information about the analyte. The response in mass spectrometric detection is based on very specific information about the analyte, i.e., the mass-to-charge ratio of the ion of interest. In the case of the perchlorate ion, the primary mass of interest is 99 based on the 75.77% relative abundance of the chlorine-35 isotope. Mass 101 is a secondary mass of interest based on the 24.23% abundance of chlorine-37. Coupled with ion chromatographic separation, mass spectrometry is by far the most promising analytical tool available today for low-level identification and quantitation of perchlorate in drinking water.⁸⁻¹¹ Typical method detection limits in waters up to 200 ppm in the common anions carbonate, chloride and sulfate, are 0.03 - 0.07 ppb with minimum reporting limits from 0.1 - 0.25 ppb. Detection limits using the secondary mass, 101, are approximately four times higher.

Currently in development at the U.S. EPA is a method that uses ion chromatographic separation of the perchlorate ion, as is done in Method 314.0, followed by electrolytic conductivity suppression prior to electrospray ionization mass spectrometric detection of perchlorate at masses 99 and 101.¹² Another approach being pursued by several commercial labs is ion chromatographic separation of perchlorate followed by electrospray ionization and MS-MS detection. In this approach, the perchlorate ion is monitored in its transition from perchlorate, mass 99, to chlorate, mass 83, after the loss of an oxygen atom in a collision cell.¹³ Both these MS methods are sensitive and specific for perchlorate at sub-ppb levels in drinking water matrices. Additionally, the same sample clean-up and concentration procedures used to improve detection limits of EPA Method 314.0 and to extend its application to more complex matrices can also be used to improve the MS methods. In the event that perchlorate is regulated in drinking water or that a second national

occurrence survey is conducted under the Unregulated Contaminant Monitoring Rule (UCMR), this current research will result in an inherently more sensitive and specific MS methods that can be readily implemented by most analytical laboratories.

1. Urbansky, E.T.; "Quantitation of perchlorate ion: practices and advances applied to the analysis of common matrices," Crit. Rev. Anal. Chem., 2000, (30), 4, pp. 311-343.
2. Low Concentration Method for the Determination of Perchlorate in Aqueous Samples Using Ion Selective Electrodes - Letter of Findings, submitted by Earth Tech, Inc, to the U.S. Army Corps of Engineers-Sacramento District, Contract No. DACA05-96-D-003, ask Order 0062, May 25, 2001.
3. Determination of Perchlorate by Ion Chromatography, Rev.0, California Department of Health Services, June 3, 1997.
4. U.S. EPA Method 314.0 Determination of Perchlorate in Drinking Water Using Ion Chromatography, Rev.1, EPA 815/B/99/003,1999.
5. Jackson, P.E.; S. Gokhale, T. Streib; J.S. Rohrer and C.A. Pohl, "Improved method for the determination of trace perchlorate in ground and drinking waters by ion chromatography," J. of Chrom. A, 2000, (888) pp. 151-158.
6. Personal Communication with Nora Conlon, U.S. EPA Region 1, Aug. 20, 2002.
7. Yongjian, L.; S. Mou and S. Heberling, "Determination of trace level bromate and perchlorate in drinking water by ion chromatography with evaporative preconcentration technique," J. of Chrom. A, 2002, 956, pp. 85-91.
8. Minter, M. and P. Winkler, "Innovations in Perchlorate Analysis by HPLC-MS/MS," presentation at 12th Annual Quality Assurance Conference, U.S. EPA Region 6, Sept 12, 2002.
9. Flaherty, J.; K. Risha; E. Decker and E. Wickremesinha, "Analysis of Perchlorate in Drinking Water and Human Serum by LC-MS/MS," Exygen Research, State College, PA, poster reprint, conference unknown.
10. Clewell, R.A.; et al, "Analysis of trace level perchlorate in drinking water and ground water by electrospray mass spectrometry," Environ. Sci. Res., (57) 2000, Perchlorate in the Environment, Editor E.T. Urbansky, pp. 31-36.
11. Urbansky, E.T.; B. Gu; M.L Magnuson; G.M. Brown and C.A. Kelty, "Survey of bottled waters for perchlorate by electrospray ionization mass spectrometry and ion chromatography," J. of the Sci. of Food and Agriculture, 2000, (80), pp. 1798-1804.

12. Schnute, William, "Environmental Applications: Ion Chromatography-Mass Spectrometry," presentation, U.S. EPA, Cincinnati, Ohio, May 30, 2002.
 13. General Engineering Labs, LLC, "Definitive Low Level Analysis Using Liquid Chromatography Mass Spectrometry/Mass Spectrometry (LC/MS/MS) by SW-846 Method 8321 Modified (8321M)," Standard Operating Procedure GL-OA-E-056 Revision 1, October, 2002.
- cc Annie Jarabek
Thomas Behymer
David Munch